

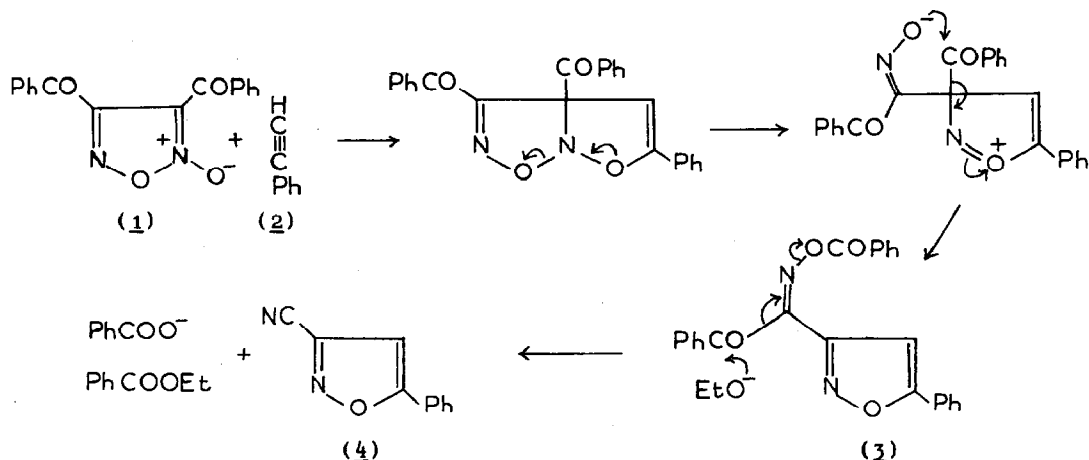
THE REACTION OF DIBENZOYLFUROXAN WITH PHENYLACETYLENE,  
STYRENE AND STILBENE

by M. Altaf-ur-Rahman, A.J. Boulton\*, and D. Middleton

(School of Chemical Sciences, University of East Anglia, Norwich)

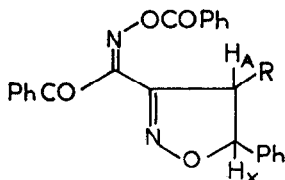
(Received in France 10 July 1972; received in UK for publication 13 July 1972)

Dibenzoylfuroxan (1) was refluxed 4 hr. in xylene with phenylacetylene (2), with a view to trapping any phenylglyoxalonitrile oxide (PhCO.CNO) which may be formed as a result of cleavage of the heterocyclic ring. On cooling the solution, fine, colourless needles were deposited, of m.p. 145-6° (70%). This product showed (i.r.) two carbonyl bands at 1766 and 1674 cm.<sup>-1</sup>, and evidently was not the expected 3-benzoyl-5-phenylisoxazole. Analytical and mass spectral data, and a logical mechanism for its formation, led to the structure of the 1 : 1 addition product, 3-(1'-benzoyloximino-2'-oxo-2'-phenylethyl)-5-phenylisoxazole (3), to be assigned to this compound.<sup>1,2</sup> Base-induced decomposition of 3, as indicated, gave the known<sup>3</sup> nitrile 4.



The reaction of dibenzoylfuroxan with styrene (6 hr. in refluxing xylene, with added quinol) gave the corresponding  $\Delta^2$ -isoxazoline<sup>1</sup> 5 (35%) in a similar way. The n.m.r. spectrum of 5 (isoxazolinic protons at  $\tau_A$  6.45,  $\tau_B$  6.0,  $\tau_X$  4.2

p.p.m.;  $J_{AB}$  -17,  $J_{AX}$  9,  $J_{BX}$  11 Hz) confirmed the location of the phenyl group at the 5-position. Stilbene similarly gave the diphenyl derivative <sup>1</sup>6 (25%) (isoxazolinic protons at  $\tau_A$  5.15,  $\tau_X$  4.45 p.p.m.;  $J_{AX}$  7.5 Hz).



(5), R = H<sub>B</sub> : m.p. 126-7°

(6), R = Ph : m.p. 125-7°

Furoxans have not previously been shown to behave as nitrones in 1,3-dipolar cycloaddition reactions. However, C-acyl nitrones are known to show unusual reactivity towards dienophiles<sup>4</sup>, as also do nitronic esters containing electron-withdrawing substituents, such as the isoxazoline-N-oxides investigated by Tartakovskii et al.<sup>5</sup> The formation of the nitrile 4 suggests that, under some circumstances at least, the very easily-prepared<sup>6</sup> dibenzoylfuroxan can be an alternative synthetic starting material to the intractable cyanogen monoxide of ref. 3.

#### References and Footnotes

- <sup>1</sup> Satisfactory analytical and mass spectral data were obtained for all new compounds.
- <sup>2</sup> We are grateful to Professor R. Huisgen for suggesting this structure.
- <sup>3</sup> C. Grundmann and H.-D. Frommelt, *J. Org. Chem.* **31**, 4235 (1966).
- <sup>4</sup> R. Huisgen, H. Hauck, H. Seidl, and M. Burger, *Chem. Ber.* **102**, 1117 (1969).
- <sup>5</sup> V.A. Tartakovskii, I.E. Chelnov, S.S. Smagin, and S.S. Novikov, *Izv. Akad. Nauk SSSR., Ser. Khim.*, 583 (1964); *Chem. Abstr.* **61**, 4335 (1964).
- <sup>6</sup> A.F. Holleman, *Ber.* **20**, 3359 (1887). H.R. Snyder and N.E. Boyer, *J. Amer. Chem. Soc.* **77**, 4233 (1955).